Supporting Information for

A copper(II)-based MOF film for highly efficient visible-light-driven hydrogen production

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Contents:

Section A. Materials and characterizations

All the reagents in this work were used as received without further purification. Copper nitrate ($Cu(NO_3)_2 \cdot 3H_2O$, 98%), trimesic acid (H_3BTC, 99%), eosin Y, triethanolamine (TEOA), ethanol (EtOH) and N, N-Dimethyl formamide (DMF) were purchased from Sinopharm Chemical Reagent Co. Ltd.. Tributylmethylammonium methyl sulfate (MTBS) was purchased from J＆K Scientific Company. Nickel foam and titanium sheet was bought from Kunshan AinuoSen Electronics Co. Ltd. and Baoji Tianshengtai Metal Co. Ltd., respectively. De-ionized water was used.

Powder X-ray diffraction (PXRD) patterns of the samples were collected with monochromatized Cu-Kα ($\lambda = 1.54178$ Å) incident radiation by a Shimadzu XRD-6000 instrument operating at 40 kV voltage and 50 mA current. Fourier transform infrared (FT-IR) spectra were recorded with KBr pellets in the range 400-4000 cm^{-1} on a Nicolet 170 SXFT/IR spectrometer. Photocatalytic hydrogen production process was carried out with a photocatalytic device manufactured by Beijing Aulight Co. Ltd., with a 300 W Xe lamp (420 nm $\leq \lambda \leq$ 700 nm) as light source. The amount of H_2 production was measured by a Shimadzu gas chromatography.

Section B. Experimental section

Preparation of MOF-199/Ni and MOF-199/Ti

For the electrodeposition experiments, $Cu(NO_3)_2 \cdot 3H_2O$ (0.9664 g, 4 mmol), H_3BTC (0.8406 g, 2.84 mmol) and MTBS (1.2459 g, 4 mmol) were dissolved in DMF solution (80 mL), which was shaken vigorously to obtain a homogeneous solution. Prior to use, nickel foam and titanium sheet (1 mm in thick) were rinsed with acetone, de-ionized water and EtOH, subsequently. The nickel foam or titanium sheet (2 cm × 1 cm × 1 mm) working electrode was partially immersed in the deposition bath, with a Pt sheet as the counter electrode. Bulk electrolysis was carried out at -1.5 V for 120 s. After that, the film was thoroughly washed by EtOH to remove the excess copper salt, ligand and MTBS.

Preparation of MOF-199

$Cu(NO_3)_2 \cdot 3H_2O$ (0.242 g, 1 mmol) and H_3BTC (0.300 g, 1.428 mmol) were dissolved in a mixed solvent of $DMF/EtOH/H_2O$ (v/v/v = 1:1:1, 90 mL) in a 150 mL round-bottom flask under mechanical stirring. The reaction mixture was stirred for 12 h. After that, the product was collected by centrifugation and washed with the above mentioned mixed solvent (20 mL × 3) and EtOH (20 mL × 3). After dried at 60 °C for 3 h, blue powder was collected.

Mott-Schottky experiment

Mott-Schottky experiment was performed by using an electrochemical analyzer (CHI 660C Instruments) in a standard three-electrode system with the as-prepared MOF-199 powders loaded on a glassy carbon electrode (diameter 3 mm) as the working electrode, a carbon electrode as the counter electrode, and saturated calomel electrode (SCE) as the reference electrode. Aqueous KCl solution (1 M) was used as the electrolyte. The working electrode was prepared as followed: 5 mg of MOF-199 was suspended in 1 mL of solution (containing 700 μL H_2O, 270 μL ethanol and 30 μL 5 wt% Nafion aqueous). 10 μL of the resulting colloidal dispersion was dropped onto the glassy carbon electrode after ultrasonication for 10 min. The conduction band of MOF-

199 was derived from the obtained Mott-Schottky plots.

Photocatalytic hydrogen production experiments

The obtained MOF-199/Ni film was hanged on the surface of water, while powdered MOF-199 catalyst was dispersed in water to form a turbid suspension. The quality of MOF-199 on the nickel foam was ca. 5 mg. To make a fair comparison, the amount of powdered MOF-199 used as catalyst was also 5 mg. The hydrogen production experiments were carried out in 50 mL 0.5 M NaH_2PO_4/K_2HPO_4 buffer solution (adjusted to different pH), with eosin Y (1 mM), TEOA (10%, v/v), and H_2PtCl_6 (co-catalyst Pt 0.5 mg, if added).

Cycle tests

The durability tests were carried out with a time interval of 3 hours for each cycle. After each cycle, eosin Y, the photosensitizer, was supplemented.

Leaching tests

Leach liquor was collected by filtration of the suspension after a nine-hour-long hydrogen production experiment. Elemental analysis by ICP was used to determine the mass of copper dissolved in the leach liquor as well as the original one in the catalyst. Hydrogen production experiments under identical conditions were also performed on the leach liquor to evaluate the contribution of the leaching species.
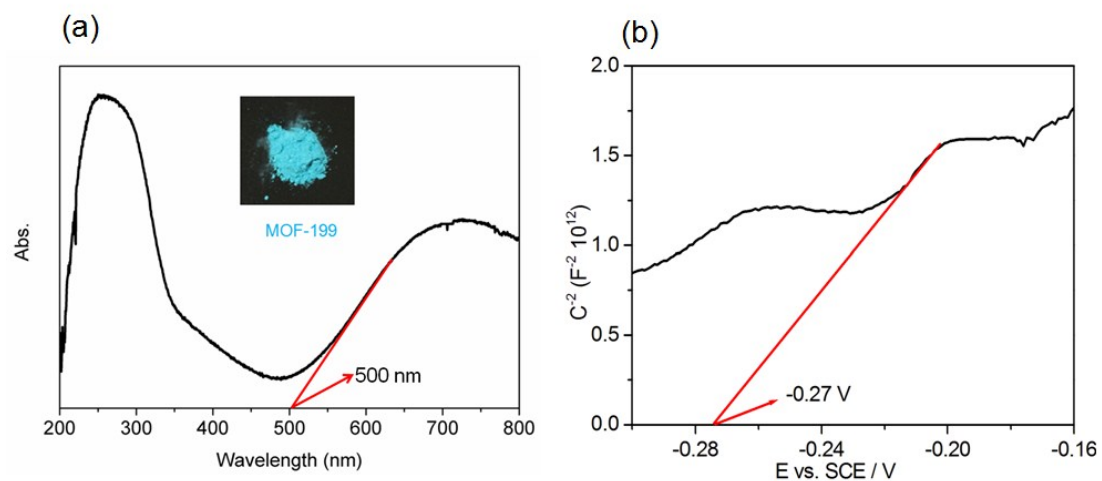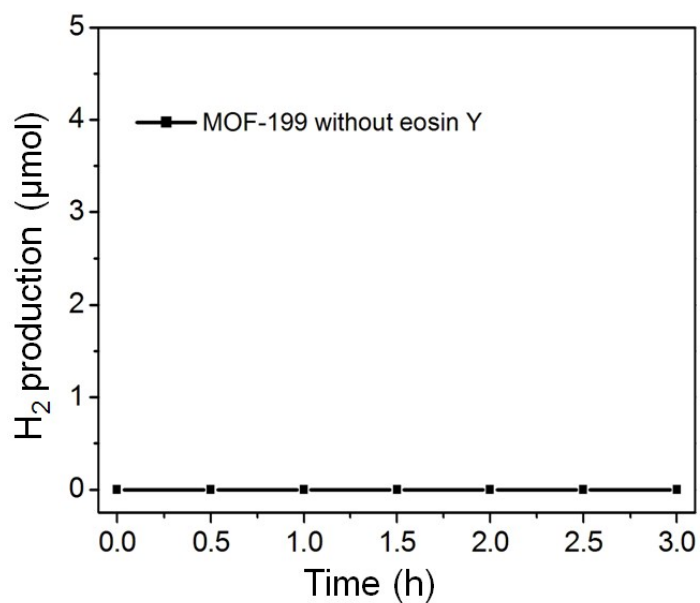
Section C. Supplementary Figures S1-S7
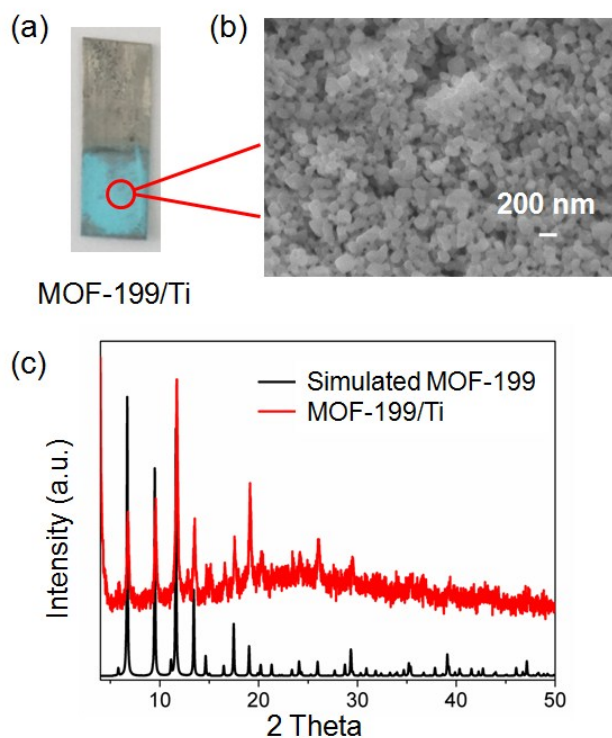
Fig. S1 (a) Optical photograph, (b) SEM image and (c) PXRD pattern of the MOF-199/Ti film prepared by electrodeposition.
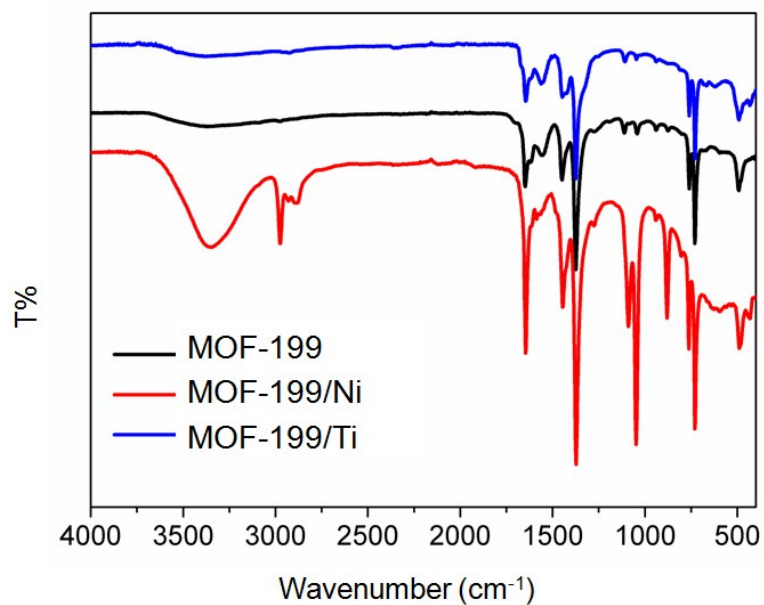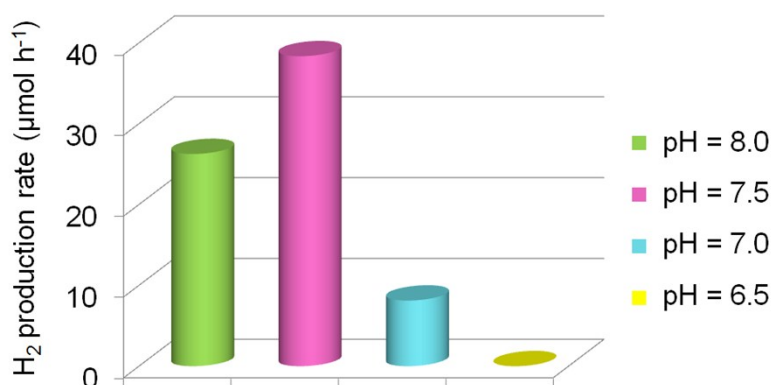

Fig. S2 FT-IR spectra of MOF-199 (black), MOF-199/Ni (red) and MOF-199/Ti (blue).

Fig. S3 (a) Solid-state UV-vis spectrum and (b) Mott–Schottky plots of MOF-199.
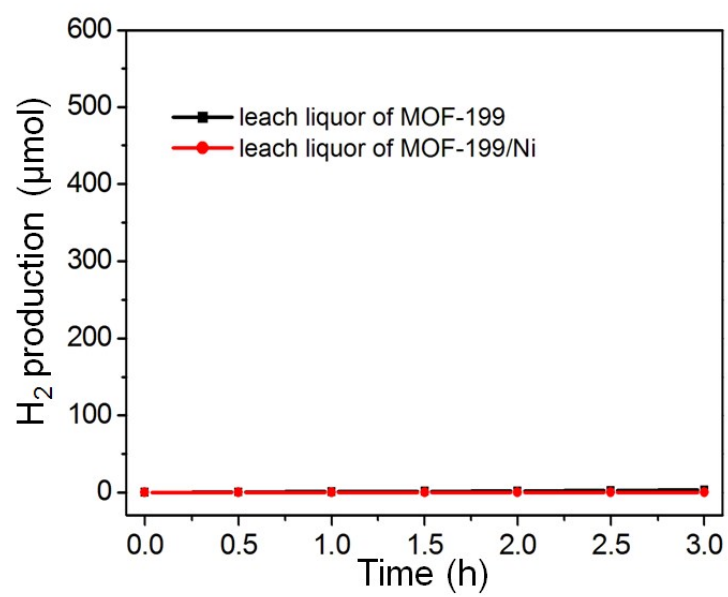

Fig. S4 Photocatalytic hydrogen production of MOF-199 without eosin Y as photosensitizer. Experiment conditions: MOF-199 5 mg, buffer solution 50 mL, pH = 7.5, 10% TEOA, 420 nm $\geq \lambda \geq$ 700 nm.

Fig. S5 Photocatalytic hydrogen production rates of MOF-199 in buffer solutions with different pH values. Experiment conditions: MOF-199 5 mg, buffer solution 50 mL, 1 mM eosin Y, 10% TEOA, 420 nm $\geq \lambda \geq$ 700 nm, without Pt.
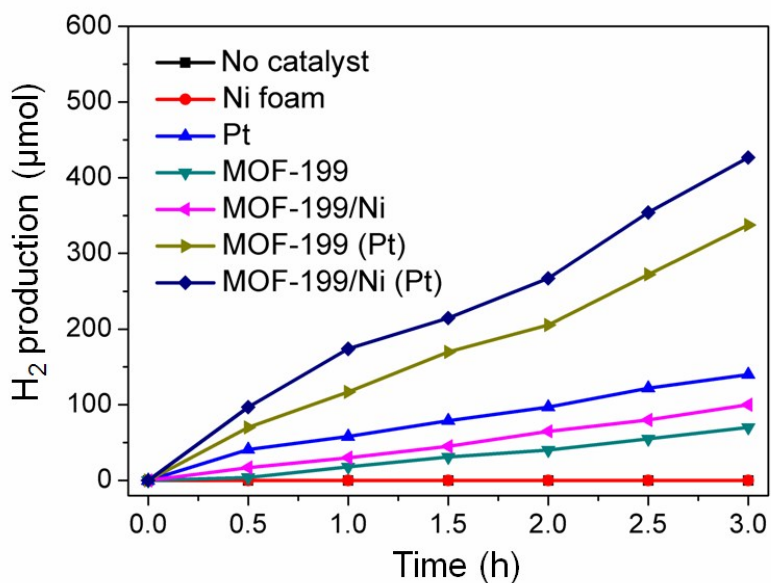
Fig. S6 Photocatalytic hydrogen production of the materials presented in this work. Experiment conditions: MOF-199 (if added or containing) 5 mg, buffer solution 50 mL, pH = 7.5, 1 mM eosin Y, 10% TEOA, Pt (if added) 0.5 mg, 420 nm $\geq \lambda \geq$ 700 nm.

Fig. S7 Photocatalytic hydrogen production of the leach liquor. Experiment condition: 420 nm $\geq \lambda \geq$ 700 nm.

Table S1. MOF-based photocatalytic systems for hydrogen production.

Photo-catalyst	Catalyst mass (mg)	Co-cat. Pt	Hydrogen production (μmol h^{-1} g^{-1})	TON	Time (h)	TOF (per hour)
Ru$_2$(p-BDC^b)$_2$ [1]	10	absence	1610	Ru-TON^g: 8.2	4	2.0
UiO-66(NH$_2$) [2]	45	1 wt%	924	Zr-TON^g: 1.2	3	0.4
		absence	178	/	/	/
Cu-RSH^c [3]	5	absence	7880	Cu-TON^g: 253.0	5	50.6
CdS@MIL-101 [4]	20	0.5 wt%	7500	Cr-TON^g: 20.0	1	20.0
Co@NH$_2$-MIL-125 (Ti) [5]	5	absence	7160	Co-TON^g: 30.0	70	0.4
Pt@Zr$_6$(μ_3-O)$_4$(μ_3-OH)$_4$(bpdc^d)$_{5.94}$(L$_1^e$)$_{0.06}$ [6]	/	/	/	Pt-TON^g: 147.0	24	6.1
Pt@Zr$_6$(μ_3-O)$_4$(μ_3-OH)$_4$(L$_2^f$)$_6\cdot$64DMF [6]	/	/	/	Pt-TON^g: 308.0	24	12.8
Pt@CdS/UiO-66 [7]	5	0.5 wt%	47000	Zr-TON^g: 25.5	1	25.5
Ni foam^a	526	absence	4	/	/	/
MOF-199^a	5	absence	7200	/	/	/
MOF-199/Ni^a	5	absence	8000	Cu-TON^g: 45.0	3	15.0
MOF-199 (co-cat. Pt) ^{a}	5	10 wt%	22000	/	/	/
MOF-199/Ni (co-cat. Pt) ^{a}	5	10 wt%	24400	Cu-TON^g: 266.0	3	88.7

[a] Present in this work; [b] p-BDC: 1, 4-benzenedicarboxylate; [c] RSH: rhodamine-based carboxylate linker by using rhodamine 6G, hydrazide, and 3-formyl-4-hydroxybenzoic acid; [d] BPDC: biphenyldicarboxylate; [e] L$_1$: chlor(η^5-pentamethylcyclopentadienyl)(2-(4-carboxyl)phenyl-(5-carboxyl) pyridine-C^2, N')iridium(III); [f] L$_2$: bis(4-phenyl-2-pyridine)(5, 5-di(4-carboxyl-phenyl) -2, 2'-bipyridine) iridium(III) chloride; [g] TON = (molar of hydrogen atom/molar of metal activity sites).

Table S2. Elemental analysis of Cu.

Mass of Cu (μg)	MOF-199/Ni	MOF-199
Initial raw material	1586	1600
Leach liquor after photocatalytic hydrogen production	77	95

Section D. Turnover number frequency (TOF) and solar to hydrogen (STH) conversion efficiency calculations

TON = molar of evolution hydrogen atom/molar of cooper activity sites.
TOF = molar of hydrogen atom/molar of cooper activity sites × time (per hour).

During 3 h of illumination, the total incident power over 1 cm^2 irradiation area was 0.13 W, so that the total input energy in 3 hours was:

$$E_{Solar} = 1.404 \times 10^3 \text{ J}$$

During the photocatalytic reaction, 450 μmol H$_2$ was detected by gas chromatography (GC), which indicated that the energy generated by water splitting was:

$$E_F = 450 \times 10^{-6} \times 6.02 \times 10^{23} \times 2.46 \times 1.609 \times 10^{-19} = 107.2 \text{ J}$$

Where 2.46 eV is the free energy of water splitting.

STH = (Energy of generation of hydrogen by water splitting)/(Solar energy irradiating the reaction cell)

$$STH = E_F/E_{Solar} = 107.2 \text{ J}/1.404 \times 10^3 \text{ J} = 7.6\%$$

Section F. References

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